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# PATENT SPECIFICATION

776,469



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## COMPLETE SPECIFICATION

### Process and Apparatus for the Electrolytic Deionisation of Salt-Containing Liquids

We, NEDERLANDSE ORGANISATIE VOOR TOEGEPAST - NATUURWETENSCHAPPELIJK ONDERZOEK TEN BEHOEVE VAN NIJVERHEID, HANDEL EN VERKEER, of 12, Koningskade, The Hague, The Netherlands, a body corporate organised under the laws of The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the deionisation and concentration of liquids and particularly to the deionisation or demineralisation of water. More particularly the invention relates to a process and apparatus for the deionisation of liquids wherein an input of ionic liquid is separated into a deionised liquid and a concentrate, in such a manner as to permit continuous use and operation over long periods of time.

The deionisation of liquids and in particular the demineralisation of water is a problem of steadily growing importance.

A well-known deionisation method is separation of salt from water by distillation in which the water is first vapourised and then condensed to yield a distillate of a low mineral content. This method, although frequently used, is costly.

A second method of deionisation involves the use of ion-exchanging substances or materials, such as cation and anion exchangers, employed in series, as by passing water first through a bed of cation exchanger and then through a bed of anion exchanger. Alternatively, the water can be passed through a single bed comprising a mixture of the two types of exchanger, a so-called "mixed-bed" ion exchanger. A drawback of this method is that the ion-exchangers used must be regenerated periodically, and that per equivalent of removed salt at least an equivalent of acid and alkali is required.

For some applications use is made of ion-exchangers which are capable of exchanging

their sodium ions for other metal ions such as calcium, thus giving a water which is "soft" instead of "hard".

These ion exchangers must be regenerated regularly, there is need for special materials and equipment, and they inherently involve a period of shutdown in the softening process.

Finally, electrodialysis is employed to an ever-increasing extent for the deionisation of ionic liquid; this process is continuous, but when the solutions are dilute, very much energy is required for the deionisation owing to the high resistance, so that this process is not suitable for obtaining highly demineralised liquids.

The present invention provides a process for the deionisation of an ionic liquid, which comprises adsorbing the ions from this liquid by an anion-exchanger and a cation exchanger disposed between two ion-permeable membranes and deionising the exchangers by applying an electric current across the membranes and the exchangers which causes displacement of adsorbed cations and anions through the membranes to a rising solution on the other side of the membranes for regeneration of said exchangers.

The invention also provides deionisation apparatus, comprising an anion exchanger and a cation exchanger, disposed in a deionisation chamber bounded on two sides by ion-permeable membranes, said chamber being provided with means for the introduction and discharge of the liquid to be deionised and the deionised liquid respectively, each membrane forming a boundary between the deionisation chamber and a rinsing chamber provided with means for the introduction and discharge of rinsing liquid, means being provided for maintaining a potential difference across the membranes and the deionising chamber.

In carrying out the invention ionic liquids are passed through cation-exchangers and anion-exchangers, present between ion-permeable membranes, preferably cation-selective and anion-selective exchanger membranes res-

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pectively, while maintaining an electric potential across the exchangers and the membranes, whereby the anions and cations are separately removed at opposed sides of the deionisation chamber.

The apparatus of the invention can be regarded as being a three- or multi-cell electro-dialysis apparatus in which an anion-exchanger and a cation-exchanger are present in the deionising chamber or chambers between the membranes. The apparatus can also be employed as a concentration apparatus for recovering costly ions from highly diluted solutions. It will be understood that if the quantity of rinsing liquid is small in proportion to the quantity of liquid deionised in the deionising chamber, the ions will form a more concentrated solution in the rinsing liquid so that concentration then takes place.

Some embodiments of the apparatus according to the invention are illustrated in the accompanying drawings, in which:—

Fig. 1 is a diagrammatic vertical sectional view of a deionising apparatus according to the invention, the electro-dialysis chamber being filled with a mixture of anion and cation exchangers, and

Fig. 2 is a diagrammatic view of a portion of an apparatus as shown in Fig. 1, but wherein the deionising cell contains alternating horizontal strata of anion and cation exchange resin.

Fig. 3 is a portion of a diagrammatic horizontal section of a cell, showing a stratum of anion exchanger and a stratum of cation exchanger present in the cell parallel to the membranes, and

Fig. 4 is a diagrammatic section of an apparatus, as indicated in Fig. 3, comprising more than one deionising chamber.

In Figs. 1—3, reference numeral 1 represents the anode, positioned in anode chamber 3; 2 is the cathode in the cathode chamber 4. The anode chamber is provided with an inlet for electrode rinsing liquid 7 and with an outlet 8; the cathode chamber with an inlet 9 and outlet 10.

The deionising chamber 5, provided with an inlet 11 and an outlet 12, is filled with ion exchangers, which are separated by ion-permeable membranes 19, 20 from the adjoining rinsing chambers. In the embodiment illustrated in Fig. 1, a mixture of ion exchangers is present between the membranes; in the embodiment according to Fig. 2 separate strata of anion exchanger 15 and cation exchanger 16 are present; the separating surfaces between the strata are here parallel to the current direction. In the embodiment according to Fig. 3 there are also separate strata of the two exchangers; the separating surface is here parallel to the membranes. Preferably membrane 19 is anion-selective and membrane 20 cation-selective.

The electro-dialysis apparatus as shown in

Fig. 4 comprises an anode 1 and cathode 2, separated by alternate anion-permeable membranes 21 and cation-permeable membranes 22. Rinsing liquid enters the anode chamber 3, containing the anode 1, through an inlet 7 and leaves through an outlet 8; liquid enters the cathode chamber 4, containing the cathode 2, through an inlet 9 and leaves through an outlet 10.

The liquid to be deionised is fed to the deionising cells 5 via duct 11, which liquid leaves the apparatus via duct 12. These cells are filled with alternate strata of cation exchanger 16 and an anion exchanger 15 in the direction of flow of the liquid. Rinsing liquid is fed to the intermediate rinsing cells 6 through duct 13, which rinsing liquid may be the same as the liquid to be deionised, and a concentrate is discharged through duct 14.

The membranes can be made of materials such as the material known under the Registered Trade Mark "Cellophane", parchment or porous ceramic substances, which are permeable to both cations and anions. Better results are obtained, however, if the membranes are of the perm-selective type. If a deionising chamber filled with an ion exchanger is bounded by a cation-selective membrane and an anion-selective membrane, ions are indeed removed from the deionising chamber but no or only a few ions are conveyed from the rinsing chambers to the electro-dialysis chamber; as in the case of an electro-dialysis apparatus with ion-selective membranes.

The thickness of the membranes is not very important, provided they are sufficiently ion-permeable and the resistance is not too high. Thus the membranes can be of a thickness to withstand the pressure differences which may exist between the deionising chamber and the adjoining chambers or suitable reinforcement can be employed to support and stiffen these relatively thin membranes.

The cation exchanger and anion exchanger can be various commercially available synthetic resins which are employed in "mixed bed" deionisation mentioned earlier. In general the sulphonic acid type cation exchangers and the strongly basic anion exchangers, e.g. those deriving their exchange capacity from quaternary ammonium groups, are found to be preferable as regards exchange capacity and rate of ion migration in an electric field.

The cation and anion exchangers can be employed in the hydrogen and hydroxyl form respectively or in the salt form. If an apparatus is filled with the sodium form of a cation exchanger and the carbonate form of an anion exchanger and hard water is passed through this apparatus at a rate faster than electro-dialytic removal of ions takes place, the exchangers may temporarily exchange the sodium and carbonate ions for other hardness-

producing ions to yield a softened water. On the other hand, if the electrodialysis is carried on for some time without flow of water through the resin bed or if the rate of flow is sufficiently slow, the water fed to the bed can be completely deionised.

It will be apparent, therefore, that the process and apparatus can be particularly adapted to deionisation of water at a uniform rate as well as to deionisation when the demand of deionised water is intermittent, since the exchanger present has a spare capacity. In the latter case it is necessary to provide a quantity of exchanger sufficiently large to handle the expected peak load on the usual ion exchange principle. In handling such a peak load the resins may become substantially saturated with adsorbed or exchanged ions. At the same time under the influence of the electric field part of the adsorbed ions migrate to the rinsing chambers. During the periods of no demand, i.e. when little or no water is passed through the exchangers the adsorbed ions are partially or wholly removed, as the influence of the electric field causes the adsorbed ions to migrate through the permeable membranes, the exchangers being regenerated.

The potential difference across the electrodes and the current strength depend on the same factors as in a normal electrodialysis apparatus, viz., on the number of cells, the salt concentration in the dialysate and in the rinsing liquid, the resistance of the membranes, the width of the cells, and the like, but particularly with a dialysate with a small salt content, the voltage is considerably lower than with a normal electrodialysis apparatus, since the resistance of the dialysate chamber is considerably lower owing to the presence of the ion exchangers.

The resistance varies according to the size and arrangement of the exchanger particles. With a relatively small particle size there is closer contact between the particles of the same exchanger than with particles of larger size, thus tending to reduce the resistance. The lowest resistance is obtained by arranging the exchangers in alternate strata; the stratification of the two exchangers is more favourable than the use of a mixture of the two exchangers.

One of the distinct advantages of the process and apparatus according to the invention is the lack of attention required after installation. Besides, the apparatus for softening or deionising water can operate efficiently and unattended for months or even years. The cost of electricity is low. The power cost will of course depend on the degree of deionisation.

The size of an apparatus depends on the salt content of the untreated water and the reduction desired and also on the peak load to be expected.

## EXAMPLE

Soil water of the following composition:— 65

Cl <sup>-</sup>	-	-	-	25	mg/litre	
SO <sub>4</sub> <sup>11</sup>	-	-	-	10	"	
HCO <sub>3</sub> <sup>1</sup>	-	-	-	74	"	
CO <sub>2</sub>	-	-	-	23.4	"	
SiO <sub>2</sub>	-	-	-	26	"	70
NH <sub>4</sub> <sup>+</sup>	-	-	-	0.1	"	
Fe	-	-	-	10.0	"	
Mn	-	-	-	0.19	"	
Ca <sup>++</sup>	-	-	-	20.6	"	
Mg <sup>++</sup>	-	-	-	3.5	"	75
Na <sup>+</sup>	-	-	-	16.2	"	

thus containing 2.56 milli-equivalents of cations per litre and having a specific resistance of 5.680  $\Omega/\text{cm}^2$  is to be deionised to a concentration of 0.0256 milli-equivalents of salt per litre (spec. resistance 560,000  $\Omega/\text{cm}^2$ ). The average specific resistance of the dialysate in the deionising cell is 26,400  $\Omega/\text{cm}^2$ ; the specific resistance of the dialysate chamber (cell width 1 mm) and 2 membranes approx. 3,100  $\Omega/\text{cm}^2$ . If the current density is 1 mA/cm<sup>2</sup>, the voltage required per dialysate chamber and 2 membranes is 3.08V. The voltage across the rinsing chambers and electrode chambers (containing concentrated solution) can be neglected with a multicell apparatus. 85

2.534 Gm. equivalents/m<sup>3</sup> metal ion must be removed; at a current yield of 50%, taken on a Coulomb basis,  $2 \times 2.534 \times 96,500 = 489,062$  Amp.sec. are required involving a power consumption of 0.42 kWh per m<sup>3</sup>. 95

If in such a deionising cell a stratum is provided with alternate strata of anion exchanger Dowex 2 (a polystyrene-divinyl benzene co-polymerisate, containing quaternary ammonium groups, the nitrogen being linked to two methyl and one hydroxy-ethyl group) and cation exchanger Dowex 50 (a co-polymerisate of polystyrene and divinyl benzene, sulfonated in the core), the average specific resistance over the same range of deionisation is only 3,000  $\Omega/\text{cm}^2$ . In this case it is, however, impossible in actual practice to maintain a cell width of only 1 mm for which reason it must be enlarged to 2 mm. 100

The resistance of the cell, including 2 membranes, averaged 740  $\Omega$  per cm<sup>2</sup>; for the deionisation of 1 m<sup>3</sup> water with a current density of 1 mA/cm<sup>2</sup> and the same current yield only 0.10 kWh was required. 105

It is remarked that with solutions containing over approximately 10 milli-equivalents of salt per litre, the difference in resistance between a normal cell and a cell which has been filled with an ion exchanger is only relatively small, so that with such a solution the use of the apparatus and the process of the invention does not offer special advantages. 120

With a dilute electrolyte solution the conductivity decreases substantially in proportion 125

to the concentration. However, this is no longer the case for the combination of dilute solutions with an ion exchanger and in this case the conductivity does not fall below a certain limit. So if concentrated solutions are to be deionised to a very low salt concentration it is preferred first to deionise electrolytically as long as the liquid has yet a sufficient conductivity and to carry out the latter part of the deionising process in an apparatus according to the invention.

What we claim is:—

1. Process for the deionisation of an ionic liquid which comprises adsorbing the ions from this liquid by an anion exchanger and a cation exchanger disposed between two ion-permeable membranes and deionising the exchangers by applying an electric current across the membranes and the exchangers which causes displacement of adsorbed cations and anions through the membranes to rinsing solution on the other side of the membranes for regeneration of said exchangers.

2. Process as claimed in Claim 1, wherein the liquid to be deionised is brought into contact with an anion exchanger and a cation exchanger arranged in strata.

3. Process for the deionisation or concentration of ionic liquids substantially as described with reference to the example.

4. Deionising apparatus, comprising an anion exchanger and a cation exchanger disposed in a deionisation chamber bounded on two sides by ion-permeable membranes, said chamber being provided with means for the introduction and discharge of the liquid to be deionised and the deionised liquid respectively, each membrane forming a boundary between the deionisation chamber and a rinsing chamber provided with means for the introduction and discharge of rinsing liquid, means being provided for maintaining a potential difference across the membranes and the deionising chamber.

5. Apparatus as claimed in Claim 4, wherein an anion selective membrane is present on the anode side of the deionising chamber and a cation-selective membrane on the cathode side.

6. Apparatus as claimed in Claim 4 or 5, wherein the anion exchanger and cation exchanger are present as separate strata.

7. Deionising apparatus substantially as described with reference to the accompanying drawings.

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Fig. 1.

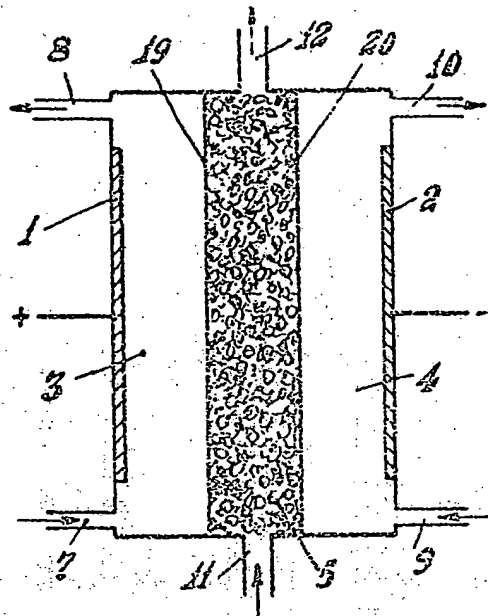


Fig. 2.

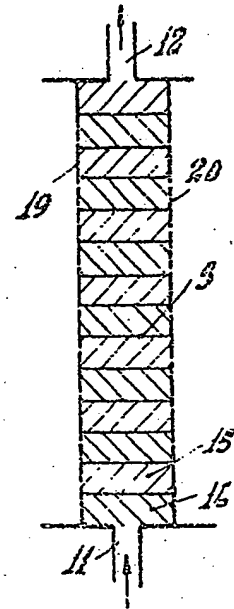
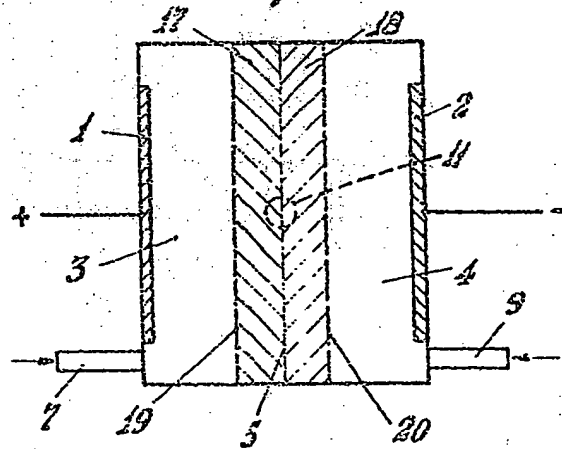


Fig. 3.



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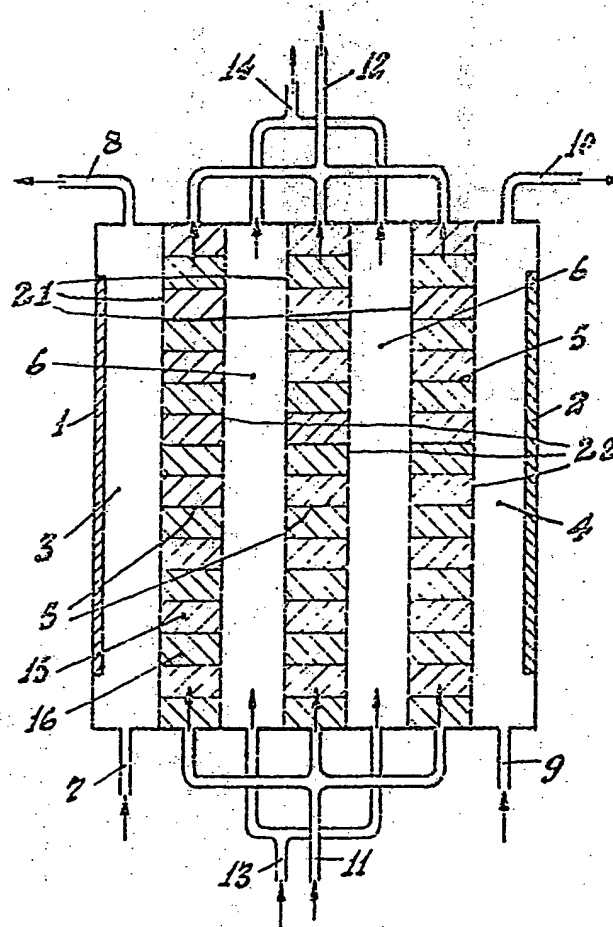
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SHEETS 1 & 2

*Fig. 4.*





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 SHEETS 1 & 2

Fig. 1.

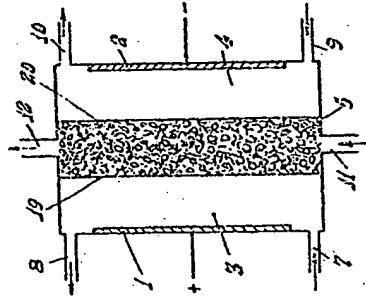


Fig. 2.

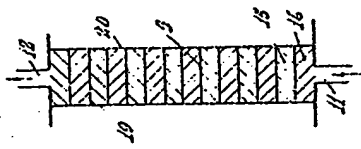


Fig. 3.

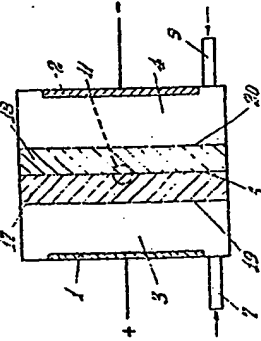
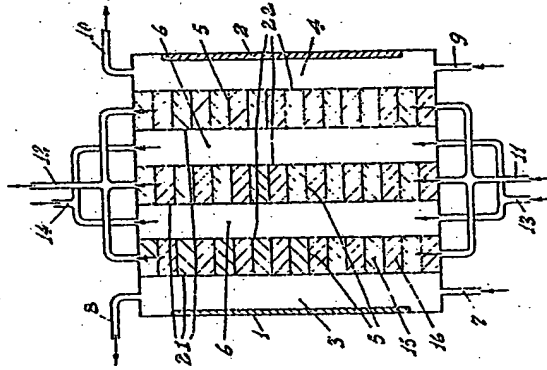


Fig. 4.



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